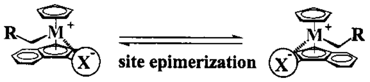
Strong Ion Pairing Effects on Single-Site Olefin Polymerization: Mechanistic Insights in Syndiospecific Propylene Enchainment

Ming-Chou Chen and Tobin J. Marks*

Department of Chemistry
Northwestern University
Evanston, Illinois 60208-3113

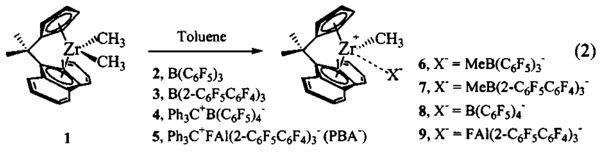
Received June 26, 2001

Although there is considerable circumstantial evidence that ion pairing has significant consequences for single-site polymerization catalyst[1] activity, lifetime, stability, chain-transfer characteristics, and stereoregulation,[2] actual mechanistic structure−function connections have remained ill-defined. In principle, the accepted pathway for syndiospecific propylene enchainment by C_s-symmetric catalysts should be a particularly sensitive probe of cocatalyst/counteranion[2,3] effects since olefin enchainment necessarily occurs in concert with “chain-swinging” (eq 1, R = polypropylene fragment).[4] It is known that rates of similar reorganization processes are sensitive to, and one metric of, ion pairing strength in model metallocenium systems (R = H, alkyl group),[3,5] and thought that analogous “back-skipping” processes without concomitant enchainment are a major source of polypropylene stereoerrors (Scheme 1).[4] Herein we communicate the first systematic study of counteranion effects on propylene enchainment stereochemistry by the archetypical C_s-symmetric precatalyst [$Me_2C(Cp)(fluorenyl)$]$ZrMe_2$ (**1**),[6] using a fairly broad array of structurally/coordinatively diverse counteranions[3] as a function of temperature, propylene pressure, and solvent polarity. It will be seen that effects can be large and are to a significant degree understandable in terms of established trends in ion pairing strength and dynamics.[7]



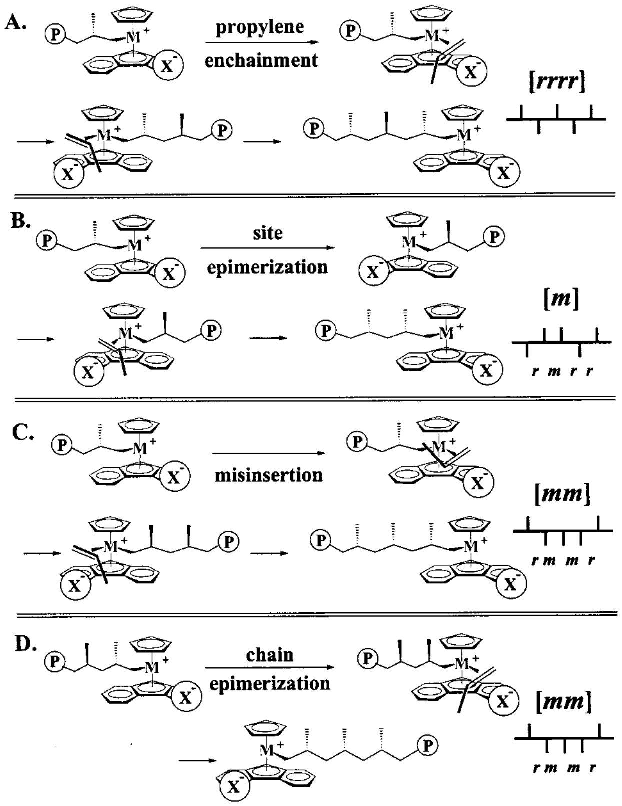
(1)

Under rigorously anhydrous/anaerobic conditions, **1** was activated with the perfluoroaryl borane, borate, and fluoroaluminate reagents shown in eq 2. Polymerizations were first carried out under 1.0 atm propylene pressure in toluene from −10° to + 60 °C using conditions minimizing mass transfer and exotherm effects;[3e,f,5] product isolation and characterization utilized standard techniques.[5b,8,9] Several trends are evident in the data (Table 1, Figure 1). Product polydispersities are consistent with well-defined single-site processes and are rather temperature-, anion-insensitive. Polymerization rates are highly anion-sensitive, with the most strongly (PBA$^-$)[5b] and weakly ($MeB(2\text{-}C_6F_5C_6F_4)_3^-$, $B(C_6F_5)_4^-$)[2a,b,5d] coordinating anions generally affording the lowest and highest polymerization rates, respectively. Not surprisingly,[1,4] product molecular weights fall with rising reaction temperature, although the superiority of strongly coordinating PBA$^-$ might not, a priori, be predicted. Most interesting, however, is the pattern in polypropylene stereoerrors ([*m*], [*mm*]) as a function of anion and temperature (Figure 1C), and which are concentration-invariant over a 32-fold range in a control experiment with **6**.[8] It can be seen that the PBA$^-$ catalyst exhibits far higher syndiotacticity, with far lower [*m*] and somewhat lower [*mm*] stereoerrors. As temperature is increased, all systems exhibit a precedented erosion in syndiotacticity,[10] however that of the PBA$^-$ catalyst is least, with the principle factor being greater temperature insensitivity of the [*m*] stereoerrors versus that of the other anions. Interest-



1

Scheme 1



---

[1] For recent reviews, see: (a) Gladysz, J. A. Ed. *Chem. Rev.* **2000**, *100*, 1167−1682. (b) Marks, T. J.; Stevens, J. C., Eds. *Top.Catal.* **1999**, *7*, 1−208. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447. (d) Jordan, R. F.; Ed. *J. Mol. Catal.* **1998**, *128*, 1−337.

[2] (a) Chen, Y.-X.; Marks, T. J. in ref 1a, pp 1391−1434, and references therein. (b) Luo, L.; Marks, T. J. in ref 1b, pp 97−106.

[3] For recent cocatalyst studies, see: (a) Chen, Y.-X.; Kruper, W. J.; Roof G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745−746. (b) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223−237. (c) Chase, P. A.; Piers, W. E.; Patrick, B. O. *J. Am. Chem. Soc.* **2000**, *122*, 12911−12912. (d) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560−9561. (e) Sun, Y. M.; Metz, M. V.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 1625−1627. (f) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312−1316.

[4] (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. in ref 1a, pp 1253−1345. (b) Coates, G. W. in ref 1a, pp 1223−1252. (c) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573. (d) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.

[5] (a) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358−10370. (b) Chen, X.-Y.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287−6305. (c) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772−1784. (d) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842−857.

[6] Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **1993**, *445*, 111−114.

[7] Presented in part at the 221st ACS National Meeting, San Diego, CA, April 1−5, 2001, Abstract INORG 65.

[8] See Supporting Information for full experimental details.

[9] NMR assay: see ref 4 and references therein.

[10] For **1**/MAO, syndiotacticity falls with increasing temperature,[10a] while for C_1-symmetric catalysts, isotacticity sometimes increases with increasing temperature:[10b] (a) Kleinschmidt. R.; Reffke, M.; Fink, G. *Macromol. Rapid Commun.* **1999**, *20*, 284−288. (b) Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A. *J. Mol. Catal. A: Chem.* **1999**, *140*, 225−233.

10.1021/ja011558p CCC: $20.00

Table 1. Propylene Polymerization Results with **1** + Indicated Cocatalysts[a]

entry	cocat (cat)	T_p (°C)	act[b] ($\times 10^4$)	*rrrr*[c] (%)	*rmmr* (%)	*mmrr* (%) ([*mm*])	*rrmr* (%) ([*m*])	M_w[d] ($\times 10^3$)	M_w/M_n
1	**2 (6)**	−10	3.1	90.0	1.1	2.2	2.2	79.8	1.75
2	**3 (7)**	−10	58	93.3	1.1	2.2	0.6	201	1.83
3	**4 (8)**	−10	920	94.0	1.0	1.9	0.6	229	1.95
4	**5 (9)**	−10	1.8	96.5	0.7	1.5	0.0	290	1.86
5	**2 (6)**	25	44	69.4	1.5	3.1	10.6	79	1.81
6	**3 (7)**	25	350	83.6	1.5	3.1	4.1	101	1.85
7	**4 (8)**	25	890	83.8	1.4	3.0	4.2	112	1.95
8	**5 (9)**	25	20	91.0	1.3	2.6	1.3	147	1.85
9	**2 (6)**	60	25	30.0	3.5	6.8	21.1	11.9	2.38
10	**3 (7)**	60	100	48.3	2.5	5.3	16.7	53.1	1.82
11	**4 (8)**	60	80	47.0	2.6	5.3	17.2	55.8	1.82
12	**5 (9)**	60	2.5	71.0	1.9	3.9	8.6	66.5	1.95
13	**2 (6)**	60[e]	18	53.8	2.5	5.1	14.7	33.9	1.89
14	**3 (7)**	60[e]	30	71.3	2.0	4.6	7.9	58.6	1.81
15	**4 (8)**	60[e]	37	73.6	2.0	4.0	7.4	63.2	1.68
16	**5 (9)**	60[e]	5.8	81.0	1.8	3.9	4.3	70.8	1.76
17	**2 (6)**	25[f]	266	49.5	2.0	4.1	18.0	97.6	1.76
18	**3 (7)**	25[f]	86	49.8	2.0	4.0	17.6	93.3	2.24
19	**4 (8)**	25[f]	453	50.3	1.9	4.2	17.3	104	1.92
20	**5 (9)**	25[f]	96	49.5	2.0	4.4	17.8	127	1.78

[a] Under 1.0 atm of propylene in 50 mL of toluene with precise polymerization temperature control (exotherm < 3 °C). See Supporting Information for full experimental details. [b] Units: g polymer/(mol cat.× atm × h). [c] Pentad analysis by ^{13}C NMR. [d] GPC relative to polystyrene standards. [e] Under 5.0 atm of propylene. [f] Under 1.0 atm of propylene in 50 mL of 1,3-dichlorobenzene.

ingly, [*mm*] stereoerrors are far less temperature-sensitive, with the PBA$^-$ catalyst again slightly superior. In contrast, the $MeB(C_6F_5)_3^-$ catalyst exhibits the lowest syndiotacticity with greatest increase of [*m*] and [*mm*] with rising polymerization temperature.

Experiments at increased propylene pressures reveal general increases in syndiotacticities (Figure 1D) and generally uniform but modest increases in product molecular weights[8] (Table 1, entries 13−16), arguing that chain-transfer to monomer[4,11] is a significant but probably not the only termination pathway. Interestingly, increases in [*rrrr*] and declines in [*m*] with increased propylene pressure are smallest for the PBA$^-$ catalyst. The stereochemical consequences of increasing [propylene] are usually ascribed to increased enchainment rates versus those of competing, tacticity-degrading site epimerization (Scheme 1B).[4,11a] Finally, polymerizations were carried in 1,3-dichlorobenzene ($\epsilon = 5.04$) (Table 1), with the net result being *compression* in the dispersion of polymerization rates and *collapse* of [*rrrr*], [*m*], and [*mm*] % to experimentally indistinguishable values of 50, 17.5, and 4%, respectively, *for all cocatalysts*.[8]

These results suggest a mechanistic picture in which anion-specific ion pairing effects modulate not only the rate of enchainment and chain transfer, but more importantly, the *relative rates* of enchainment versus [*m*]-enhancing/syndiotacticity-degrading site epimerization (Scheme 1B).[12] More tightly bound, stereochemically immobile anions should depress epimerization rates,[5] with computational studies arguing that propagation in nonpolar media involves concerted anion displacement and monomer enchainment rather than highly endergonic unimolecular ion pair separation.[13] To the extent that rates of dynamic NMR-quantifiable unimolecular reorganization processes (detected by averaging of magnetically diastereotopic sites)[5] in $[Me_2C(Cp)(fluorenyl)]ZrMe^+X^-$ ion pairs mirror barriers in eq 1, we find that the PBA$^-$ ion pair indeed has by far the highest barrier ($\Delta G^\ddagger \geq 25$ kcal/mol vs 19.5 (2) kcal/mol for $MeB(C_6F_5)_3^-$).[14] Other NMR and crystallographic data support the strong coordinative properties of PBA$^-$.[5b] In contrast to these results, misinsertion or chain epimerization[4c] processes producing [*mm*] stereoerrors (Scheme 1 C and D) would not appear to be directly influenced by decoupling from chain-swinging, and indeed it is found that the low level of [*mm*] is far less anion-dependent although, interestingly, these results show that the ion pairing does affect enantiofacial discrimination and chain epimerization as well (Figure 1C).[15] Last, spectroscopic,[5] theoretical,[13] and polymerization studies[16] argue that polar solvents significantly weaken ion pairing in other single-site systems, and in accord with a picture that ion pairing modulates syndiospecific enchainment, we find here that differential anion effects on propagation rates diminish[8] and those on stereoerrors *completely vanish* in a more polar solvent.

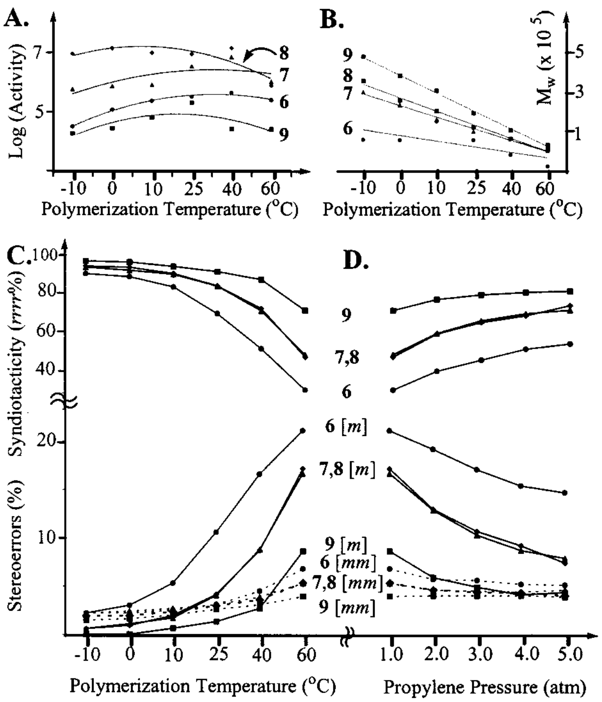


Figure 1. (A) Polymerization activity, (B) polypropylene molecular weight, and (C) pentad distribution (%) data for polypropylenes produced by **1** + indicated cocatalysts under 1.0 atm of propylene from −10° to 60 °C. (D) Pentad distribution (%) data for polypropylenes produced by **1**+ indicated cocatalysts as a function of propylene pressure at 60 °C. Lines connecting data points are drawn as a guide to the eye.

Acknowledgment. Financial support by DOE (DE-FG02-86ER1351) is gratefully acknowledged. M.-C. C. thanks Dow Chemical for a postdoctoral fellowship, Dr. L. Li for helpful discussions, and Dr. P. Nickias of Dow for GPC measurements.

Supporting Information Available: Details describing syntheses of **6**−**9**; polymerization experiments and polymer characterization; tables of pressure- and solvent-dependent polymerization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA011558P

---

(11) (a) For C_s catalysts, lower propylene concentrations correlate with lower product molecular weights and tacticities (mostly [*m*]-type stereoerrors).[4c] (b) In contrast, declining isotacticity with increasing monomer concentration is observed in C_1 catalysts: Kukral, J.; Lehmus, P.; Feifel, T.; Troll, C.; Rieger, B. *Organometallics* **2000**, *19*, 3767−3775. (c) For another recent monomer concentration study, see: Lin, S.; Tagge, C. D.; Waymouth, R. M.; Nele, M.; Collins, S.; Pinto, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11275−11285.

(12) For general kinetic models, see: (a) Bravakis, A. M.; Bailey, M. P.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000−1009. (b) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771−3778.

(13) (a) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764−12777. (b) Lanza, G.; Fragalà, I. L. in ref 1b, pp 45−60. (c) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257−8258. (d) Chan, M. S. W.; Ziegler, T. *Organometallics* **2000**, *19*, 5182−5189, and references therein.

(14) (a) Line broadening is found to be independent of concentration over an 8-fold range for **6**. (b) For **7** and **8**, extensive thermal decomposition occurs at > 80 °C. (c) In *o*-xylene-d_{10}.

(15) The weak pressure dependence of %[*mm*] argues for a misinsertion origin.

(16) (a) Herfert, N.; Fink, G. *Makromol. Chem.* **1992**, *193*, 773−778. (b) Coevoet, D.; Cramail, H.; Deffieux, A. *Makromol. Chem. Phys.* **1999**, *200*, 1208−1214.